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Mechanical and Thermophysical Properties of Mg3TH7 (T= Mn, Tc, Re) Complex Hydrides

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ABSTRACT

The Mg_3TH_7 (T= Mn, Tc, Re) compounds are hexagonal ternary complex hydrides. The characteristic features of high-temperature ternary complex hydrides are investigated by the theoretical evaluation of thermophysical and ultrasonic properties at room temperature using interaction potential model approach. From elastic constants calculations, it is noted that Mg_3MnH_7, Mg3TcH7 and Mg_3ReH_7 brittle. With the help of second order elastic constants other elastic moduli, elastic stiffness constants and Poisson's ration are estimated at room temperature for elastic and mechanical characterization. The ultrasonic velocities and thermal relaxation time of these ternary complex hydrides are evaluated utilizing evaluated values of elastic constants and lattice parameters within the same physical conditions. The orientation dependent ultrasonic velocities and thermal relaxation time have been also evaluated for the determination of anisotropic behaviour and thermophysical properties. The obtained results are analyzed to explore the characteristic of complex hydrides compounds.

Keywords: Ternary Complex Hydrides, Elastic Properties, Ultrasonic Velocity, Thermal Relaxation Time

I. INTRODUCTION

Ternary complex transition hydrides have been considered to be very attractive candidates and have received significant attention as hydrogen storage materials. These compounds show a higher capacity for hydrogen storage in volume densities than compressed gaseous and liquid hydrogen [1]. In recent decades, research and development of new hydrogen storage materials opened up new possibilities for industrialists. On the other hand, the major challenges in solid state hydrogen storage are improved energy storage density, faster kinetics, and improved cycle life, using readily available elements at reasonable costs, with particular reference to fuel cells and rechargeable batteries [2, 3]. Matar et al. [4] have investigated the electronic structure and bonding of three different complex hydrides Mg3MnH7, Mg3ReH7 and Mg3TcH7 by the pseudo- potentials and computation of all electrons within the DFT. They have shown that both Mg3MnH7 and Mg3ReH7 have desorption energies within the range of MgH2 and are higher than those of covalent-like hydrogenated intermetallic compounds. The complex hydrides Mg3MnH7 and Mg3ReH7 compounds crystallize in hexagonal P63/mmc [5, 6].

In the present work, we have worked diligently to make the relationship between thermo physical and

microstructural properties for hexagonal Mg3TH7 (T= Mn, Tc, Re) complex hydrides. Mg3TH7 (T= Mn, Tc, Re) complex hydrides will help in understanding the mechanical behaviour of complex hydrides and it will play an important role in the diagram of industrial equipment with useful physical properties under moderate operating conditions. For that, we have considered elastic constants, stiffness constant, thermal relaxation time and ultrasonic velocity for complex hydrides. Young's modulus (Y), bulk modulus (B), shear modulus (G), Pugh's ratio (B/G), Poisson's ratio (σ) has also been evaluated and discussed for these complex hydrides.

II. METHODS AND MATERIAL

In this work, the interaction potential model approach has been used for the calculation of higher order elastic constants. The formulations of higher order elastic constants have been obtained by the second or third order strain derivatives of elastic energy density. The second (CIJ) and third (CIJK) order elastic constants of material are specify by following expressions.

$$C_{IJ} = \frac{\partial^2 U}{\partial e_I \partial e_J}; \qquad I \text{ or } J = 1,.....6 \qquad (1)$$

$$C_{IJK} = \frac{\partial^3 U}{\partial e_I \partial e_J \partial e_K}; I \text{ or } J \text{ or } K = 1,.....6 \qquad (2)$$

where, U is elastic energy density, eI=eij (i or j = x, y, z, I=1, …6) is component of strain tensor. Eqs. (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal structure materials [7, 8].

$$\left.\begin{array}{ll} C_{11} = 24.1\,p^4C' & C_{12} = 5.918\,p^4C' \\ C_{13} = 1.925\,p^6C' & C_{33} = 3.464\,p^8C' \\ C_{44} = 2.309p^4C' & C_{66} = 9.851\,p^4C' \end{array}\right\} \qquad (3a)$$

$$\left.\begin{array}{ll} C_{111} = 126.9\,p^2B + 8.853p^4C' & C_{112} = 19.168p^2B - 1.61p^4C' \\ C_{113} = 1.924p^4B + 1.155p^6C' & C_{123} = 1.617p^4B - 1.155p^6C' \\ C_{133} = 3.695p^6B & C_{155} = 1.539p^4B \\ C_{144} = 2.309p^4B & C_{344} = 3.464p^6B \\ C_{222} = 101.039p^2B + 9.007p^4C' & C_{333} = 5.196p^8B \end{array}\right\} \qquad (3b)$$

where p = c/a: axial ratio; $C' = \chi\, a / p^5$; $B = \psi\, a^3 / p^3$; $\chi = (1/8)[\{nb_0 (n-m)\}/\{a^{n+4}\}]$ $\psi = -\chi/\{6\, a^2 (m+n+6)\}$; m, n=integer quantity; b0=Lennard- Jones parameter

Calculations of bulk modulus (B) and shear modulus (G) have been computed using Voigt and Reuss' approaches [9-12]. The Debye average velocity (VD) is well connected to longitudinal (VL) and shear wave (VS1, VS2) velocities. The expressions for ultrasonic velocities, thermal relaxation time(τ) are known in our prior papers [12, 13].

III. RESULTS AND DISCUSSION

In the current analysis we have calculate the elastic constants (six second order elastic constants and ten third order elastic constants) using the theory given by Eqn. (3) and Eqn. (4). The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for Mg3MnH7, Mg3ReH7 and Mg3TcH7 are 4.46917 Å, 4.810 Å, 4.8501 Å and 2.1843, 2.792, 2.1921 respectively [14]. The value of m and n for complex hydrides are 6 and 7. The values of b0 are 8x10-63 erg cm7, 1.07x10-62 erg cm7and 1.21x10-62 erg cm7 for Mg3MnH7, Mg3ReH7 and Mg3TcH7 compounds respectively. The calculated values of SOEC and TOEC have been calculated for these complex hydrides at room temperature are offered in Table 1.

Table1. Second and third order elastic constants (SOEC and TOEC) (in GPa) at room temperature.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B
Mg_3MnH_7	150	37	57	245	68	59	101
Mg_3MnH_7[14]	150.29	25.21	48.04	209.35	87.03	62.54	----
Mg_3TcH_7	155	38	59	255	71	61	105
Mg3TcH7 [14]	153.78	34.72	57.64	206.20	82.20	59.53	----
Mg_3ReH_7	162	39	62	268	74	63	110
Mg3ReH7[14]	161.68	36.85	59.22	215.85	86.93	62.41	-----

	C_{111}	C_{112}	C_{113}	C_{123}	C_{133}	C_{344}	C_{144}	C_{155}	C_{222}	C_{333}
Mg_3MnH_7	-2437	-386	-146	-186	-1652	-1549	-216	-144	-1928	-11082
Mg_3TcH_7	-2541	-403	-152	-194	-1722	-1614	-226	-150	-2011	-11547
Mg_3ReH_7	-264	-417	-159	-202	-1812	-1699	-236	-157	-2086	-12242

Complex hydrides had the highest elastic constant values, which are important for the material, as these are associated with the stiffness parameter. Second-order elastic constants are used to determine the ultrasonic attenuation and associated parameters. The highest elastic constant values found for complex hydrides are indicative of their better mechanical properties over other complex hydrides of the same group.

Clearly, for a steady hexagonal structure the five independent second order elastic constants (Cij, namely C_{11}, C_{12}, C_{13}, C_{33}, C_{44}) should satisfy the well-known Born- Huang's stability norms [15, 16] i.e. $C_{11} - |C_{12}| > 0$, $(C_{11}+C_{12})\,C_{33} - 2C^2_{13} > 0$, $C_{11} > 0$ and $C_{44} > 0$. It is understandable from Table-1. It is evident that the values of elastic constant are positive and satisfies the Born-Huang's mechanical stability constraints and therefore all these compounds are mechanically stable. Using the formula $B= 2(C_{11}+ C_{12}+ 2C_{13} + C_{33}/2)/9$, the bulk modulus B, for complex hydrides can be calculated and presented in Table 1. The calculated values of C_{12}, C_{13} and C_{44} are few different than some other theoretical [14] results for these complex hydrides compound. Actually Benyelloul et al. [14] were theoretically evaluated using density functional theory (DFT), which is quite different from present approach. Although obtained order of SOEC are of the same as given in Table. 1. Relative magnitude of C_{11}, C_{33}, C_{66} are well presented by our theoretical approach. Thus, there is good agreement between the presented and the reported values which is correlated with elastic constants. Thus, our theoretical approach is well justified for the calculation of second order elastic constants of hexagonal structured compounds. We present the calculated values of TOECs in table 1. The negative values of TOECs indicate a negative strain in the solid. The negative third order elastic constants appear in the previous paper on hexagonal structure material. Hence the theory applied for evaluation of higher order elastic constants, at room temperature, is justified [17, 18]. Hence the applied theory for the valuation of higher order elastic constants, at room temperature, is acceptable.

The values of Young's modulus (Y), shear modulus (G), bulk modulus (B), Poisson's ratio (σ) and Pugh's ratio (B/G) for Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides at room temperature are calculated and presented in Table 2.

Table 2. Voigt–Reus' constants (M and C^2) Bulk modulus (in $10^{10}Nm^{-2}$), Shear Modulus (in $10^{10}Nm^{-2}$), Young's Modulus (in $10^{10}Nm^{-2}$), Poisson's ratio, Pugh's ratio for Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides.

	M	C^2	B_r	B_v	G_r	G_v	Y	B/G	G/B	σ
Mg_3MnH_7	44.83	485.17	1.90	93.26	66.72	65.67	1.63	1.53	0.65	0.231
Mg_3TcH_7	46.78	524.60	1.48	97.41	69.34	68.33	1.63	1.52	0.66	0.230
Mg_3ReH_7	48.99	574.64	1.22	102.0	72.05	71.06	1.69	1.54	0.65	0.232

It is found that the value of Young's modulus, Shear modulus and Bulk modulus of Mg_3MnH_7 are smaller than Mg_3ReH_7. Thus, Mg_3MnH_7 have little Stiffness and bonding with respect to Mg_3ReH_7. Pugh's ratio (B/G) and Poisson ratio (σ) are the measure of brittleness and ductility of solid. If $\sigma=0.23\leq0.26$ and $B/G = 1.53\leq1.75$, the solid is usually brittle, otherwise

it is ductile in nature [11]. Our finding of lower values of Pugh's ratio and Poisson ratio compared to their critical values indicates that Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides are brittle in nature at room temperature. It is well known that for stable and elastic material the value of σ should be less than 0.5. It indicates that Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides are stable against shear. A stronger degree of covalent bonding leads to higher hardness. The hardness, compressibility, ductility, brittleness, toughness, and bonding nature of the material are also well connected with the SOECs.

In the present investigation, we have correlated the mechanical and isotropic behavior of the material with the ultrasonic velocity. We have calculated the longitudinal ultrasonic velocity (V_L), shear ultrasonic velocity (V_S), the Debye average velocity (V_D) and the thermal relaxation time (τ) for Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides. The data of density for these hydrides have been taken from literature [16].

The angular dependences of ultrasonic wave velocity (V_L, V_{S1}, V_{S2} and V_D) at different temperature are shown in figs. 1-4. The angles are measured form the unique axis of the crystal. Form figs. 1 and 3 the velocity V_L and V_{S2} of these complex hydrides have decreases with unique axis of the crystal and in figs. 2 and 4 it is evident that the velocity V_{S2} and V_D maxima at 55^0 and 35^0 respectively with the unique axis of the crystal. The abnormal behavior of angle dependent velocity is due to the combined effect of second order elastic constants and density. The nature of the angle dependent velocity curves in the present work is similar to the nature of angle dependent velocity curve found for other hexagonal structured material [18, 19]. Thus the angle dependence of the velocities in transition-metal disilicides is justified. As the calculation of V_D involves the velocities V_L, V_{S1} and V_{S2} [20, 21], It is understandable that the variation of V_D is affected by the constituent ultrasonic velocities. The maximum V_D at 55° is due to a significant increase in longitudinal and pure shear (V_{S2}) wave velocities and a decrease in quasi-shear (V_{S1}) wave velocity. It may be concluded that the average sound wave velocity is maximum when a sound wave travels at 55^0 angles with the unique axis of these crystal.

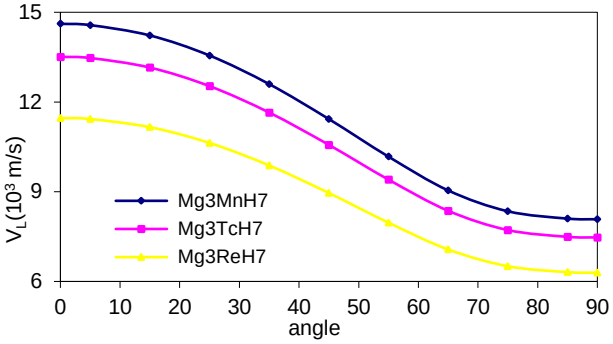

Figure 1. V_L vs angle with unique axis of crystal

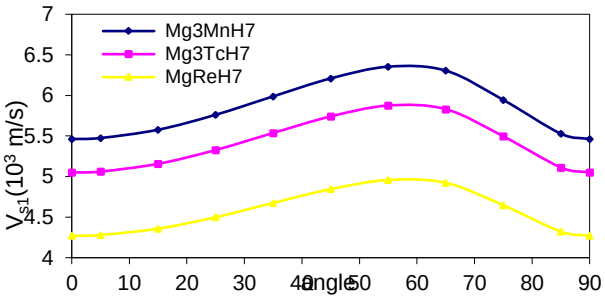

Figure 2. VS1 vs angle with unique axis of crystal

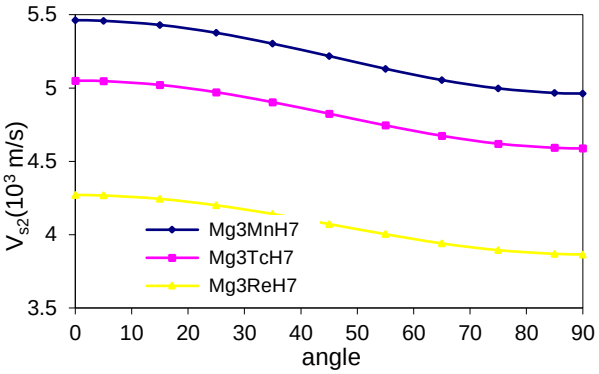

Figure 3. VS2 vs angle with unique axis of crystal

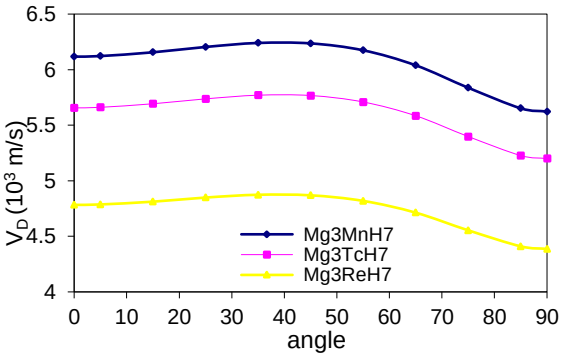

Figure 4. VD vs angle with unique axis of crystal

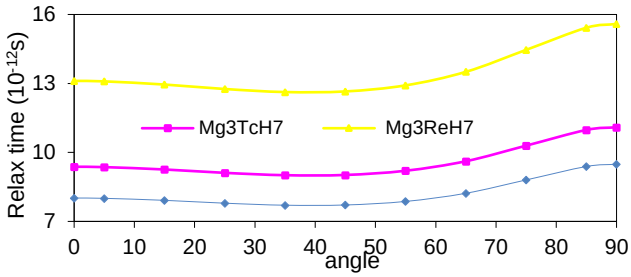

Figure 5. Relaxation time vs angle with unique axis

Fig. 5 show a that the thermal relaxation time 'τ' decreases lightly with angle up to 55^0 with unique axis of the crystal and then decreases. The angle dependent thermal relaxation time curves follow the reciprocal nature of V_D as $\tau \propto 3K / C_V V_D^2$. It is clear that thermal relaxation time for Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides is mainly affected by the thermal conductivity. For hexagonal structured material τ is of the order at picosecond to femtosecond [20, 21]. Hence the calculated 'τ' justifies the hexagonal structure of transition metal disilicides. The minimum 'τ' for wave propagation along $\theta = 55^0$ implies that the re-establishment time for the equilibrium distribution of thermal phonons will be minimum for propagation of wave along this direction.

IV. CONCLUSION

Based on the above conversation is valuable to state that:

- The principle established on simple interaction potential model remains valid for calculating higher-order elastic coefficients for hexagonally structured complex hydrides.
- At room temperature, Mg_3ReH_7 shows better mechanical properties that Mg_3MnH_7 due to larger values of stiffness and elastic constants.
- Higher order elastic constants and density for these ternary complex hydrides are mainly the affecting factor for anomalous behaviour of ultrasonic velocities.
- Mg_3TH_7 (T= Mn, Tc, Re) complex hydrides, the thermal relaxation time is found to be of the order of pico- seconds, which defends their hexagonal structure. As 'τ' has smallest value along $\theta = 55^0$ the time for re-establishment of equilibrium distribution of phonons, will be minimum, for the wave propagation in this direction

Study can be beneficial for the processing and non-destructive characterization of ternary complex hydrides. These results will provide a ground for investigating the major thermophysical properties in the field of other ternary complex hydrides.

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